

1 549 845

## PATENT SPECIFICATION

(11) 1 549 845

(21) Application No. 14011/75 (22) Filed 4 April 1975  
 (23) Complete Specification filed 25 March 1976  
 (44) Complete Specification published 8 Aug. 1979  
 (51) INT CL<sup>2</sup> C23C 9/02 9/04  
 (52) Index at acceptance  
 C7F 1B2 2A 2F 2M 2T 2Z2 2Z4 2Z8 4E 4F 4K 4X 5A  
 (72) Inventors JAMES EDWARD RESTALL and  
 CECIL HAYMAN

(54) IMPROVEMENTS IN OR RELATING TO THE  
 DIFFUSION COATING OF METAL  
 OR OTHER ARTICLES

5 (71) I, THE SECRETARY OF STATE FOR DEFENCE, London, do hereby declare the invention, for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to processes for coating metal or other articles with diffusion coatings and particularly, though not exclusively, relates to coatings for gas turbine engine components, e.g. turbine blades, for increasing their high temperature corrosion resistance.

15 It is known to produce metallide or metallised coatings by constant pressure, halide activated, pack-cementation. Aluminised and chromised coatings have been applied to nickel-based, cobalt-based and iron-based substrates by this method.

20 In a known pack-cementation process such as is described in United States Patent 3,257,230 to Wachtel, a method of coating cobalt-based or nickel-based alloys is disclosed in which a pack comprising a metallic coating material such as aluminium, chromium, iron or silicon, a carrier comprising a halide source such as ammonium halide, and a moderator metal are packed around the article to be coated and heated to between 760°C and 1204°C for 15 minutes to 40 hours. During this heating, the aluminium or other coating material is transported to the surface of the article and deposited thereon.

25 In such a process, the transport of halide vapour between the coating material and the article is primarily by diffusion, and as a consequence such a process is fairly slow and has relatively poor 'throwing power', i.e. the transport by diffusion of the halide vapours will only occur effectively over very short distances. When coating articles on their external surfaces, this poor 'throwing power' is usually not important, since by embedding the article to be coated in a particulate pack of the coating material the element which is to be transferred is in very close proximity of the article.

50 By contrast, the coating of internal surfaces such as bores is considerably more difficult to achieve by the pack cementation method. This is especially so in relation to the metallising of the surfaces of fine bores and cavities as are found for example in gas turbine engine components. United States Patent 3,079,276 and British Patent 1,315,228 describe the filling of holes and cavities of gas turbine engine components with a powder pack mix, but it is known that such practices are both difficult and time consuming to carry out and not always effective even for holes which are relatively large and of simple configuration.

55 It is also known to apply coatings of metals and compounds to internal surfaces by exposing the heated surfaces to a thermally decomposable metal plating gas such as nickel carbonyl. Such a process is described in British Patent 1,070,396.

60 The present invention provides an improved process for producing diffusion coatings on an article by metalliding or metallising and is particularly applicable to coating fine bores or narrow cavities in gas turbine engine components and other articles.

65 According to the present invention a process for coating a metal or other article with a diffusion coating comprises enclosing the article in a chamber together with a particulate pack including coating material in elemental or chemically combined form, said coating material selected from the group comprising aluminium, chromium, titanium, zirconium, tantalum, niobium, yttrium, rare earth metals, boron and silicon, together with a halide activator, and cyclically varying the pressure of an inert gas or a reducing gas or a mixture of said gases within the chamber whilst maintaining the contents of the chamber at a temperature sufficient to transfer coating metal on to the surface of the article to form a diffusion coating thereon.

70 Preferably the method according to the invention is carried out at a pressure substantially below atmospheric pressure that is,

50

55

60

65

70

75

80

85

90

5 below about 100 torr, and at a cycle frequency as high as is compatible with the transport of a sufficient quantity of the gas through the particulate pack per cycle. The ratio of upper pressure limit to lower pressure limit is preferably as high as is practicable and consistent with cycle frequency. Convenient pressure ranges are about 50 torr to about 10 torr, preferably with cycle frequencies of at 10 least 2 cycles per minute. In general, higher frequencies are beneficial in increasing the

ratio of coating thickness applied internally to that applied externally.

15 The halide activator is preferably selected from a group of inorganic halides having a low volatility at the coating temperature, such that halide loss from the chamber is low. Preferably, sufficient halide activator is used to ensure that some halide activator is retained in the pack at the end of the process. Examples of low volatility halide activators are 20 shown in Table 1.

TABLE 1

25 Equilibrium Vapour, Sublimation or Dissociation Pressures of Some Low Volatility Halide Activators

	Substance	Temp °C	Pressure torr	Substance	Temp °C	Pressure torr
	AlF <sub>3</sub>	927	1.3	LiI	827	47
	NaF	927	0.1	CrF <sub>3</sub>	785	0.01
30	NaCl	927	2.4	CrF <sub>2</sub>	927	approx 0.001
	NaBr	927	4.8	CrCl <sub>2</sub>	927	5.0
	NaI	927	15.0	CrBr <sub>2</sub>	810	0.9
35	KF	927	1.2	CrI <sub>2</sub>	793	1.4
	KCl	927	4.0	CoF <sub>2</sub>	927	0.05
	KBr	927	6.5	FeF <sub>2</sub>	927	0.02
	KI	927	12.3			

Activators of higher volatility are shown in Table 2.

40 Equilibrium Vapour, Sublimation or Dissociation Pressures of Some High Volatility Activators

	Substance	Temp °C	Pressure torr	Substance	Temp °C	Pressure torr
45	Cl <sub>2</sub>	-34	760	NH <sub>4</sub> Br	397	760
	Br <sub>2</sub>	61	760			
	I <sub>2</sub>	183	760	AlCl <sub>3</sub>	180	760
	HCl	-167	760	AlBr <sub>3</sub>	225	760
	HBr	-35	760	AlI <sub>3</sub>	385	760
50	HI	100	760	FeCl <sub>3</sub>	319	760
	NH <sub>4</sub> F	—	760	FeCl <sub>2</sub>	934	760
	NH <sub>4</sub> Cl	397	760	BeBr <sub>2</sub>	927	570

55 The choice of halide activator must also take into account factors other than volatility. In particular, the activator must also be capable of entering into the necessary chemical equilibria which will lead to the to-and-fro gas transport and proper interaction with the coating material and the article to be coated, at the coating temperature which must not exceed the temperature at which significant degradation of the properties of the article occurs. In the case of certain nickel-base and cobalt-base alloys, for example, significant degradation can occur at coating temperatures above about 900°C. Other halides which may be used in the process of the invention are double halides for example sodium cryolite, Na<sub>3</sub>AlF<sub>6</sub>. It may also be

70 desirable to employ a mixture of halide activators, for example

NaF/NaCl/NaBr or KF/NaF/LiF to increase the efficiency of the deposition process.

75 When producing aluminised coatings by the method of the invention, aluminium fluoride, AlF<sub>3</sub>, has been found to be particularly effective, good quality coatings of satisfactory uniformity and distribution having been obtained on both internal and external surfaces of nickel-base gas turbine blades. Preferably the proportions of the aluminium source material (coating material) and aluminium trifluoride are such that aluminium trifluoride crystals are not formed.

85

In one manner of operating the process in accordance with the invention, the article to be coated is kept out of physical contact with the particulate bed by placing the article to be coated inside a cage which is itself embedded within the particulate pack. A preferred construction for a cage is one that will permit vapours to pass from the particulate pack to the inside of the cage but which prevents or retards flow to the outside of the cage. One cage according to the invention has sides and an upper face of imperforate material, e.g. nickel sheet or plate, and the base of a mesh or gauze through which vapour can pass. This design has the effect of increasing the path length of the inert and/or reducing gas through the particulate bed, thereby promoting more effective entrainment of the active halide vapour.

The particulate pack may include a particulate filler such as a refractory oxide for support of the coating material or for dilution of the pack. A particulate filler comprising a refractory oxide may support a coating material such as liquid aluminium.

The articles coated by the process may be composed of any material that can be coated by pack cementation. Materials commonly coated by pack cementation are nickel-base, cobalt-base and iron-base alloys, and the refractory metals of Groups IV, V, and VI of the Periodic Table. In addition to these materials, carbon and carbon-containing materials, e.g. tungsten carbide, may be advantageously coated by the process.

An example of the process applied to aluminising and in accordance with the invention will now be described with reference to the drawing accompanying the Provisional Specification.

The drawing shows a leak-tight chamber and auxiliary plant in which the method may be carried out.

Referring to the drawing, the chamber includes a furnace tube 9 composed of mullite surrounded at its lower end by an alumina tube 5 surrounded in turn by an electrical heating element 4 and standing in a thermally insulated box 6 which has a nickel foil heat shield 7 on its upper surface. A gas turbine blade 1 of nickel-base alloy which is to be coated is located in a pack 2 comprising a powder mixture of aluminium,  $AlF_3$ , and  $Al_2O_3$  powder retained in the furnace tube 9 by an aluminium disc 3.

The furnace tube 9 is connected by a pipe 20 to auxiliary equipment for continuously varying the pressure in the tube 9. The auxiliary equipment comprises a supply of argon 26 and a vacuum pump 27 connected to the pipe 20 by time controlled valves 24, 25 and needle valves 22, 23 respectively. A mercury manometer (not shown) is connected to a branch 21 of the pipe 20 and is used for

measuring the pressure fluctuations in the furnace tube 9.

The upper part of the furnace tube 9 is closed by an end plate 19 which is bolted to a flange 10 on the furnace tube. A pair of O-ring seals 13, 14 provide gas tight sealing between the end plate 19 and the furnace tube. A screw cap 28 engages with a thread on a cylindrical part of the end plate 19 and has an O-ring seal 12 which provides a gas tight seal between the end plate and the tube 17 which extends through the screw cap 28.

The upper part of the furnace tube 9 is water cooled, the water flowing through a copper pipe 18 to the upper end of the furnace tube. A stainless steel tube 17 surrounding the tube 18 carries the return water flow. The temperature of the pack is sensed by a thermocouple (not shown).

The method according to the invention is illustrated by the following examples:—

#### EXAMPLE 1

A gas turbine blade section in 'IN 100' alloy, bearing a hole of diameter about 1.5 mm and of length about 110 mm, was aluminised according to the method of the invention in a chamber. The method included embedding the blade section in a powder mix of 14 grams  $AlF_3$ , 14 grams Al and 388 grams  $Al_2O_3$ , raising the temperature of the chamber and its contents to 900°C and setting time-controlled valves to give a flow of argon into the chamber for 3 seconds as the pressure was increased from 6 torr to 28 torr, a constant pressure of about 28 torr for 20 seconds and then an exhaust period of 7 seconds to reduce the pressure to about 6 torr. After 10 hours at the same temperature, the chamber was cooled and the blade section removed. On examination, the surface of the hole was found to be uniformly coated with an aluminised layer of mean thickness about 35  $\mu m$ . The thickness distribution of the coating along the length of the hole can be seen from the following figures:—

Distance from one end of hole (mm)	10	20	30	40	50
Coating thickness ( $\mu m$ )	40	40	35	30	30

#### EXAMPLE 2

In a further example, a turbine blade in 'IN 100' alloy bearing holes of diameter about 1.5 mm and of length about 70 mm, was aluminised for 5 hours at 900°C inside a nickel gauze cage which was itself embedded in a powder pack mix of 6.5 grams  $AlF_3$ , 10.6 grams Al and 330 grams  $Al_2O_3$ . The pressure range of argon was from 14 to 58 torr and the pressure cycle frequency was 6 cycles minute<sup>-1</sup>. Bright metallic-looking and particularly smooth textured aluminised layers

were produced on both the internal and external surfaces of the blade. The layer thickness within the hole measured close to the top, mid-span and bottom was respectively 12, 8 and 12  $\mu\text{m}$ . The layer thickness measured over the external surface at comparable positions was 25, 25 and 30  $\mu\text{m}$  respectively.

#### EXAMPLE 3

In a further example a turbine blade in 'Nimonic 105' alloy (Nimonic being a Registered Trade Mark), bearing holes of two differing cross sections, about 0.8 and 1.5 mm, but of the same length about 60 mm, was aluminised for 6 hours at 900°C inside a nickel gauze cage which was itself embedded in a powder pack mix of 6.6 grams AlF<sub>3</sub>, 10.5 grams Al and 330 grams Al<sub>2</sub>O<sub>3</sub>. The pressure range of argon was from 4 to 44 torr and the pressure cycle frequency was 6 cycles minute<sup>-1</sup>. Aluminised layers of quality similar to those obtained in the preceding example were produced on both the internal and external surfaces of the blade. The internal surface of the larger cross section hole had thicknesses of 30, 20 and 30  $\mu\text{m}$  respectively at the top, mid-span and bottom positions. The corresponding thicknesses for the smaller cross section hole was 15, 12 and 15  $\mu\text{m}$ . External thicknesses at about the same positions were 65, 60 and 60  $\mu\text{m}$  respectively.

#### EXAMPLE 4

In yet a further example of aluminising with AlF<sub>3</sub>, a turbine blade in 'MAR-M 246' alloy (MAR-M being a Registered Trade Mark), bearing holes of two different cross sections, one with major and minor axes of about 2 and 0.5 mm and the other of diameter about 2 mm, but both of length about 60 mm, were aluminised for 6 hours at 900°C inside a nickel gauze cage which was itself embedded in a powder pack mix of 6.6 grams AlF<sub>3</sub>, 10.6 grams Al and 330 grams Al<sub>2</sub>O<sub>3</sub>. The pressure range of argon was from 12 to 52 torr and the pressure cycle frequency was 6 cycles minute<sup>-1</sup>. Similar quality aluminised layers were produced on both the internal and external surfaces of the blade. The internal layer thickness along the length of the approximately elliptical section was 20, 15 and 25  $\mu\text{m}$  close to the top, mid-span and bottom positions. The corresponding figures for the circular cross section were 40, 40 and 45  $\mu\text{m}$ . Corresponding figures for the external surface were 60, 65 and 65  $\mu\text{m}$ .

#### EXAMPLE 5

In an example of aluminising with NaCl as halide activator, a turbine blade in 'IN 100' alloy was aluminised for 5 hours at 900°C within a nickel gauze cage which was itself embedded in a powder pack mix of 20 grams NaCl, 14 grams Al and 300 grams Al<sub>2</sub>O<sub>3</sub>. The pressure range of argon was from 8 torr

to 42 torr and the pressure cycle frequency was 6 cycles minute<sup>-1</sup>. A layer of thickness 2  $\mu\text{m}$  was produced within a hole of diameter 1.8 mm and of length 40 mm. The thickness of the external layer was about 16  $\mu\text{m}$ .

#### EXAMPLE 6

In an example of aluminising with NaF as halide activator, an alloy section in 'IN 100' was aluminised for 5 hours at 900°C within a nickel gauze cage which was itself embedded in a powder pack mix of 14.7 grams NaF, 13.6 grams Al and 330 grams Al<sub>2</sub>O<sub>3</sub>. The pressure range of argon was from 12 to 56 torr and the pressure cycle frequency was 6 cycles minute<sup>-1</sup>. An aluminised layer of thickness 8  $\mu\text{m}$  was produced within a hole of diameter about 1 mm and of length about 40 mm. The aluminised layer thickness over the external surface was about 30  $\mu\text{m}$ .

The process of the invention may be used to apply various types of diffusion coatings to the internal and external surfaces of articles which hitherto have been applied by conventional pack cementation processes, e.g. aluminising, chromising, titanising, tantalising, boronising and siliconising. To one skilled in the art, it will be appreciated that some activators may respond better than others to a particular metallising process, and some care must therefore be exercised in the choice of activators. Activators of low volatility that are not readily available may be synthesised within or outside the coating chamber prior to operation of the coating step and introduced into the pack. In one embodiment of the invention, SiCl<sub>4</sub> is synthesized from silicon and ammonium chloride, for use in siliconising.

#### WHAT I CLAIM IS:—

1. A process for coating a metal or other article with a diffusion coating comprising enclosing the article in a chamber, together with a particulate pack including coating material in elemental or chemically combined form said coating material selected from the group comprising aluminium, chromium, titanium, zirconium, tantalum, niobium, yttrium, rare earth metals, boron and silicon, together with a halide activator, and cyclically varying the pressure of an inert gas or a reducing gas or a mixture of said gases contained within the chamber whilst maintaining the contents of the chamber at a temperature sufficient to transfer coating material on to the surface of the article to form a diffusion coating thereon. 105
2. A process as claimed in Claim 1 in which the maximum pressure of the gas or gases is 100 torr. 110
3. A process as claimed in Claim 1 in which the maximum pressure of the gas or gases is 50 torr and the minimum pressure is 10 torr. 115
4. A process as claimed in any previous 120
- 125

claim in which the pressure of the gas or gases is cyclically varied at a rate of at least 2 cycles per minute. 25

5. A process as claimed in any previous claim in which the halide activator has a low volatility at the temperature at which said diffusion coating is formed. 30

6. A process according to Claim 5 in which the coating material comprises aluminium and the halide activator comprises aluminium fluoride. 35

7. A process according to any previous claim in which the article is held out of contact with the particulate pack. 40

8. A process according to any previous claim in which the pack includes a particulate filler for supporting the coating material. 45

9. A process according to Claim 8 in which the carrier comprises a refractory oxide. 50

10. A process according to Claim 9 in which the refractory oxide comprises aluminium oxide. 55

11. A process according to any previous

claim in which the halide activator is synthesised in the chamber. 25

12. Convert milligrams of sample/ml. of herein with reference to the Examples. 30

13. A metal article having a coating which has been coated onto said article by a process according to any previous claim. 35

14. An article composed of nickel-base alloy having a coating which has been coated onto said article by a process according to claim 6. 40

15. An article composed of iron-base alloy having a coating which has been coated onto said article by a process according to Claim 6. 45

16. An article composed of cobalt-base alloy having a coating which has been coated onto said article by a process according to Claim 6. 50

F. R. ROBINSON,  
Chartered Patent Agent,  
Agent for the Applicant.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1979  
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from  
which copies may be obtained.

1549 845

**PROVISIONAL SPECIFICATION**

1 SHEET

This drawing is a reproduction of  
the Original on a reduced scale.

